2410-2E2 (6th Quarterly Report)

Sixth Quarterly Report

INVESTIGATION OF THE REINFORCEMENT OF DUCTILE METALS WITH STRONG, HIGH MODULUS DISCONTINUOUS, BRITTLE FIBERS

by

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

May 1, 1968

CONTRACT NASw-1543

Space Sciences Laboratory
GENERAL ELECTRIC COMPANY
Missile and Space Division

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SUMMARY

This progress report covers the period from 1 February 1968 to 30 April 1968; the work is being performed under Contract NASw-1543, with Mr. James J. Gangler of NASA Headquarters serving as Program Monitor.

The purpose of this program is to define and investigate the critical factors affecting the reinforcement of ductile metals with short, brittle fibers. The materials selected for study were aluminum (or its alloys) and "ductile" epoxies reinforced with B_4C whiskers or with high modulus filaments, such as, $B_4C/B/W$*, SiC/W, B/W, etc. Related tasks in the program include the development of a more economical process for growing B_4C whiskers, the investigation of deposition parameters, the production of continuous B_4C filaments, and the characterization of the individual constituents in the final composites. The latter task involves a study of the structural and chemical interactions of the combined elements (fibers, matrix, coatings, etc.).

The results obtained during this period are summarized as follows:

1. About 13,000 feet of boron carbide-coated B/W filament was made during this reporting period. Former deposition studies had decreased the strength of the original substrate (B/W) by as much as 30%. The coating process has since been varied so that original B/W filament strengths are unaltered by the process.

A few feet of B/SiO_2 filament was also boron carbide coated. This material is of interest because of its lower density and lower inherent cost since silica glass is substituted for the tungsten core of the B/W material.

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* This terminology denotes a multiphase filament, in which B_4C is vapor deposited over a boron filament having a W-substrate core. Other filaments, such as SiC/W denote a SiC deposit on a W-substrate core, and such terminology is used throughout the text.

2. The room temperature strength properties of $B_4C/B/W$ and the $B_4C/B/SiO_2$ material was determined as a quality-control measure during the coating process. These results are presented in terms of the coating run conditions, and of their maximum, minimum and average strength properties.

3. A method was developed which allows the bond strength of filamentary materials in epoxy Novolac to be varied independent of chemical and mechanical properties of the matrix. This was accomplished by applying intermittent (porous) coatings of graphite and teflon, which are chemically inert, to the resin. A chemical approach (the addition of more plasticizer) proved impractical because of its accompanying modification of the mechanical behavior of the cured resin.

4. A sample preparation technique was developed for making aluminum - $B_4C/B/W$ composites so that they can be subsequently tested at high temperatures.

5. A generalized model has been developed to explain and predict many effects of material properties, specimen configuration and test conditions on composite performance. The concept is advanced that mechanical compatibility as well as chemical compatibility is an important attribute of successful composites and is of comparable importance.

6. A qualitative discussion of the concept of intermittent bonding and its effect on the mechanical behavior of a matrix in the vicinity of a filament break is presented in an Appendix attached to this progress report. By using stress trajectory analysis, it is shown that intermittent bonding can re-distribute stresses transferred to it through filament failure by spreading these new local stresses over a greater length of the filament. This in turn causes less stress concentration at the filament fracture site and therefore minimizes the possibility of a matrix crack.

I. INTRODUCTION

From a reinforcing viewpoint, whiskers (single-crystal fibers) appear to have many desirable characteristics. A number of classes of compounds have been prepared in this form including metals, oxides, nitrides, carbides and graphite. The strengths observed for these whiskers range from about 0.05 to 0.1 of their elastic moduli, the latter values approaching predicted theoretical strengths. Many also have relatively low densities and are stable at high temperatures. Calculations of whisker-reinforced composite properties based on whisker properties, particularly for the brittle whiskers of high modulus materials, show that they have an enormous potential compared to more conventional materials on both a strength/density and a modulus/density basis.

The incorporation of whiskers into composites requires the following series of processing steps:

(1) Whisker growth

(2) Whisker beneficiation, to separate strong fibers from the growth debris.

(3) Whisker classification, to separate according to size.

(4) Whisker orientation, to align the whiskers and maximize reinforcement along a specific axis.

(5) Whisker coating, to promote wetting and bonding.

(6) Whisker impregnation with matrix material, to form a sound strong composite.

Because of the many processing steps, there are a large number of imposing technical problems to be solved in order to achieve the high potential strengths. Many of these problems have not yet been solved.

In a few isolated cases, involving very small and carefully prepared samples, the predicted strengths of the brittle whisker/ductile matrix composites have been achieved. However, all too frequently, attempts to scale up the composites into even modest size specimens have resulted in strengths that range from about 10 to 30 percent of the predicted values.

A list of possible reasons for the low composite strength values is given in Table I. As can be seen, there are many variables to contend with, and many of these are interrelated and difficult to study experimentally.

A fundamental difficulty in evaluating the performance of whisker composites is the lack of knowledge concerning the whiskers themselves. This is understandable when one realizes that there are about 10^9 to 10^{10} of them per pound, and characterization of even a small fraction becomes a major task. These and other problems have limited the immediate use of B_4C whiskers, which had been synthesized and characterized in previous studies.[1-4].

An alternate means to gain useful, fundamental knowledge concerning whisker-reinforced composites involves the use of brittle, continuous filaments. Continuous filaments have several advantages over whiskers when investigating the reinforcement of materials; some of these advantages are listed below:

(1) It is much easier to characterized the relevent and critical parameters listed in Table I.

(2) The available continuous filaments are large relative to the whiskers and can be more readily handled and incorporated into composites.

(3) The filaments can be cut to uniform, desired lengths so that the effects of discontinuous reinforcements can be assessed.

Experimental work of this type has already been done using ductile tungsten filaments in a ductile copper[5] matrix. Although this work has provided a wealth of information regarding the reinforcement of metals, it does not uncover all of the key problems encountered with truly brittle fibers, in a ductile matrix. The chief difference between the reinforcement of metals with brittle and with ductile fibers is that the ductile fibers can deform to accommodate local, high stress concentrations, whereas brittle fibers cannot do so. Thus, it is necessary to carry out further studies and to evaluate the potential and engineering limitations of metals reinforced with brittle fibers and whiskers.

TABLE I. VARIABLES AFFECTING THE TENSILE STRENGTH OF WHISKER-REINFORCED COMPOSITES

A. Whisker Variables

1. Average strength
2. Dispersion of strength values
3. Strength versus whisker diameter and length
4. Strength degradation during handling and fabrication
5. Strength versus temperature
6. Elastic Modulus

B. Matrix Variables

7. Yield strength
8. Flow properties
9. Strength versus temperature (particularly shear strength)
10. Matrix embrittlement due to mechanical constraints and new phases formed

C. Composite Variables

11. Volume fractions of components--fiber and matrix
12. Homogeneity of whisker distribution
13. Whisker aspect ratio
14. Whisker orientation
15. Interfacial bond strength

This program was therefore initiated to investigate in detail the behavior of a ductile metal (aluminum) reinforced with various brittle fibers, such as $B_4C/B/W$, SiC/W, B/W, etc. (in both continuous and chopped lengths) to provide data which would be pertinent to whisker-reinforced metals. Included in this investigation was a parallel study using a "ductile" epoxy novolac, which in turn has led to the recognition and documentation of three failure modes possible in fiber-reinforced composite materials. This program is being conducted in two parts: (1) The development of a process to grow B_4C whiskers which would be amenable to eventual scale-up and (2) An investigation of the reinforcement of aluminum and "ductile" epoxies with brittle, high modulus filaments, such as B_4C which would simulate the B_4C whiskers.

A review of the results of the first year of effort[6] includes the following:

(1) Extensive studies were made of B_4C whisker growth systems which utilized chemical vapor deposition rather than direct B_4C bulk vaporization. These systems included boron tribromide + hydrogen + CCl_4 and the volatile substituted boranes, tributyl borane and ethyl decaborane. This approach appeared to lend itself most easily to whisker growth scale-up.

(2) A ready supply of $B_4C/B/W$ filament materials was necessary to continue composite studies. A previously developed process[7] was modified so that purchased B/W filaments could be coated with a layer of B_4C while still maintaining the high strength capability of B/W filaments. B/W filaments coated in this manner were able to withstand molten aluminum for significant times without reaction, and thus allowed liquid infiltration techniques to be used in the preparation of composites.

(3) $B_4C/B/W$ filaments were the mainstay of the filamnet-composite work. However, many other filamentary materials including, B/W, SiC/W, B/SiO_2 and W were also examined for potential usage and to document the mechanical behavior characteristics of composite materials as a function of

individual filament characteristics. A final phase of the characterization portion of this study considered the matrix-filament stability of aluminum-filament composites of the Al-B_4C/B/W and Al-SiC/W systems.

(4) Composite studies encompassed a variety of filaments utilizing "ductile" epoxy novolac resins and aluminum matrices using both single and multiple filament arrays. This work has established experimentally the critical fracture modes of an epoxy matrix in the vicinity of a break in a high modulus, high strength filament. Three distinct failure modes were observed to occur and the nature of these three modes was explained through an analysis of the stress state in the matrix [6].

(5) Continuous filament Al-B_4C/B/W composites were fabricated which showed full utilization of the strength potential of individually tested filaments in a number of instances. SiC/W-Al composites, however, suffered a large decrease in strength because of an unfavorable reaction between the filaments and a Ti/Ni coating which had been used to promote wetting.

(6) By being cognizant of the literature concerning composite mechanical behavior coupled with the present study, a tentative judgement of the expected mechanical behavior of all types of fiber composite materials was made through consideration of individual filament strength and modulus, bond strength between filament and matrix, matrix and fialment ductility, and matrix and filament mechanical response to strain rate changes.

The report contained the work performed for NASA under Contract NASw-1543 and covered the period from 1 November 1966 to 31 October 1967. However, it was decided to continue the present program under the same charter and Contract No. (NASw-1543). Thus, this progress report is #6 in the Quarterly Series.

Studies during this 6th Quarter included an assessment of the continuous processing of B_4C/B/W filaments with the objective of upgrading the strength of the resulting material. The processing technique used had decreased the strength of the original starting B/W filament material by about 30%. However, refinements have led to a B_4C coating process which results in $B_4C/B/W$ filamentary material which is at least equal to the starting substrate material. (B/W) Also, statistical evidence indicates that under ideal deposition conditions, substrate strength can be improved slightly.

The characterization of filamentary material was continued. These filaments were samples of those which were concurrently used in composite studies presented in a later section of this report.

Studies using single filament-epoxy composites containing normal B/W filaments; and exceptionally high strength B/W filaments were made to further illustrate the effects of various filament characteristics on the resultant mechanical behavior of composites. A most important variable, the "bond strength" was varied by coating with graphite. These studies are described. Multifilament composites and composites containing discontinuous filament arrays were also prepared and studied.

Since a technique has been developed which can effectively vary the bonding efficiency of epoxy novolac - B/W composites by coating the filaments with graphite (or other organic or inorganic lubricants) it has been possible to assess more fully the variables shown in Table I. A term, "mechanical compatability, has been coined to describe this analysis. These results are explained.

A qualitative discussion of "intermittent bonding" is presented in the Appendix. The significance of a bonding system which varies only as a function of filament contact area and not a chemical "bond Strength" variation is used for this discussion. It is shown by using stress trajectory analysis that the crack sensitivity of a matrix can be altered significantly when intermittent bonding is used.

II. EXPERIMENTAL PROCEDURES - RESULTS, DISCUSSION

A. PREPARATION OF CONTINUOUS BORON CARBIDE COATED FILAMENT

During the present report period, efforts were made to prepare a sufficient supply of high quality boron carbide-coated boron filament to enable composites of high volume fraction to be fabricated. Preliminary experiments were carried out to perfect deposition conditions so as to produce the highest strength coated filament. A supply of boron filament (tungsten core) of high and uniform tensile strength* was used. Variations in stoichiometry were the principle object of study in the light of previous findings which indicated that excess boron trichloride had a deleterious effect on filament tensile strength. In the course of these studies, the boron substrate was heated in each of the gas components separately to determine their individual effect on the filament strength. It was found that hydrogen also had a seriously weakening effect, so it too was held to a minimum in the gas mixture. A composition typical of that finally arrived as is as follows:

BCl_3	42 cc/min
CH_4	10 cc/min
H_2	31 cc/min

Filament temperature during deposition was also varied until a suitably high deposition rate could be obtained without weakening or burning out the filament. Figure 1 shows a view of the deposition system built to carry out the production of about 13,000 feet of boron carbide coated filament (0.2 lb.) with a minimum of down time due to shifting of traps and feed cylinders.

1. $B_4C/B/W$ Filament

Two shipments of boron substrate filament were used. The first, VAL 1124 with which the production cycle began, had a higher average strength than the second, HS 2364, although both originated from the same source. Valves determined in this laboratory are shown in Table II which is a summary of all of the production deposition runs made. The tensile strength

*Hamilton Standard Div. of United Aircraft Corp., Windsor Lock, Conn. 06096.

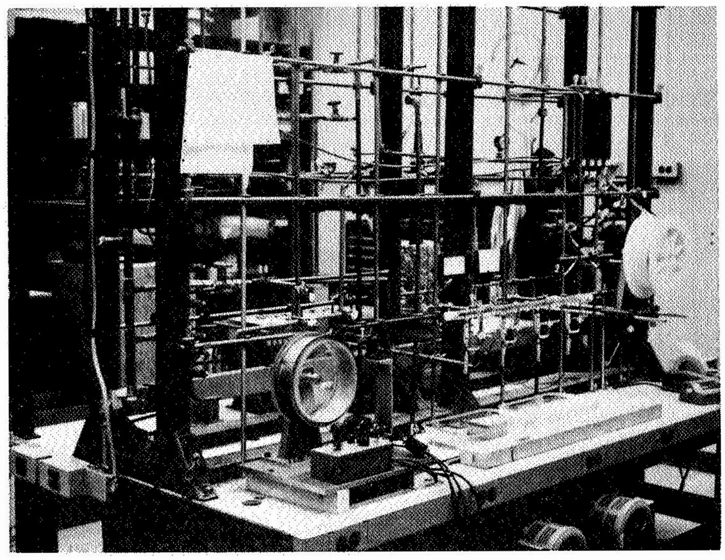

Figure 1. View of Continuous Deposition Apparatus for Boron Carbide on Boron

of HS 2364 after coating was almost universally lower than that of UAL 1124 after coating by an amount which renders it unsatisfactory for routine use. After a short production period with this reel, the UAL 1124 material was substituted and tensile strengths returned to their former values, which characterized the UAL 1124 reel at the outset of the deposition series. A change in boron process conditions by the supplier may be responsible. With this particular batch of substrate, and in the absence of splices, the deposition ran virtually untended until the traps were filled and required transfer to the feed line.

The filament obtained is similar to that which has been previously described. Because of the changes made in stoichiometry of the feed gas, the coatings appeared to be slightly thinner. On occasion, for reasons as yet undetermined, there are what may be bare places. It would appear that either because of gas fluctuations, or because of a surface nucleation anomaly, only boron rather than boron carbide was deposited. It is speculated

TABLE II. BORON CARBIDE PRODUCTION DATA

Conditions:
Temperature 1215-1280 as noted (Pyrometer)
Pressure: 1 atmosphere
Speed: two feet per minute
Gas Feed Rate: BCl_3 42 cc/min
H_2 31 cc/min
CH_4 10 cc/min
Reactor: Single Stage, 6" long, Parallel Feed
Substrate: Boron on Tungsten. Source: Hamilton Standard Div., United Aircraft Corp.

Run #	Date	# of feet/run	Substrate Identity	°C	(inches) Diameter Orig.	Final	Tensile Strength KPSI Hi	Lo	Avg	Modulus Meg PSI	Reason for Termination and Remarks
1	3/8/68	29.25	1124	1250	.0038	---	---	---	---	---	splice
2	3/8/68	29.25	1124	1275	.0038	---	---	---	---	---	wavy filament
3	3/8/68	13.00	1124	1250	.0038	---	---	---	---	---	wavy filament
4	3/18/68	270	1124	1270	.0038	---	---	---	---	---	splice; wavy filament
5	3/18/68	42	1124	1270	.0038	.0039	550	420	488	58.5	
6	3/19/68	20	1124	1215	.0038	---	---	---	---	---	change traps
7	3/19/68	616	1124	1220	.0038	.004	640	500	571	54.2	
			1124	1265	.0038						
8	3/20/68	206	1124	1240	.0038	.004	580	75	403	---	splice
9	3/20/68	300	1124	1225	.0038	.004	665	460	612	58.9	
10	3/21/68	472	1124	1265	.0038	.004	590	79	429	54.0	bend in substrate
11	3/21/68	120	1124	1250	.0038	.004	611	151	488	---	
12	3/22/68	690	1124	1250	.0038	.0041	605	398	504	53	splice
13	3/22/68	210	1124	1250	.0038	.0042	612	246	466	---	
14	3/25/68	760	1124	1180	.0038	.0043	606	48	425	51.8	
			1124	1220	.0038						
			1124	1285	.0038						
15	3/26/68	650	1124	1265	.0038	---	---	---	---	---	clogged CH_4 meter
16	3/26/68	30	1124	1285	.0038	---	---	---	---	---	fresh BCl_3
17	3/26/68	120	1124	1285	.0038	---	---	---	---	---	replace BCl_3 bottle
18	3/26/68	150	1124	1285	.0038	.0042	600	36.2	249	53	
19	3/27/68	660	1124	1205	.0038	.0042	640	51	462		
			1124	1240	.0038					51.8	
			1124	1295	.0038						

TABLE II. BORON CARBIDE PRODUCTION DATA (Cont'd.)

Run #	Date	# of feet/run	Substrate Identity	°C	(inches) Diameter Orig.	Final	Tensile Strength KPSI Hi	Lo	Avg	Modulus Meg PSI	Reason for Termination and Remarks
20	3/28/68	610	1124	1255	.0038	---	---	---	---	---	clogged CH_4 meter
21	3/28/68	258	1124	1280	.0038	.00415	608	45	314	52.9	slight back pressure
22	3/29/68	140	1124	1275	.0038	.0043	410	59	295	54.4	splice
			HS								
23	3/29/68	780	2364	1275	.004	.00425	575	71	407	51.8	
24	4/1/68	720	2364	1255	.004	---	---	---	---	---	trap change
25	4/1/68	390	2364	1255	.004	.0043	548	48	283	55.8	
26	4/2/68	450	2364	1285	.004	---	---	---	---	---	CH_4 meter clogged
27	4/2/68	300	2364	1260	.004	---	---	---	---	---	splice
28a	4/2/68	106	2364	1285	.004	.00415	534	74	341	52.9	stop to get sample
28b	4/2/68	174	2364	1280	.004	.0042	558	25	373	51.9	slight back pressure
29	4/3/68	320	2364	1235	.004	.0042	506	116	402	51.7	weak break
30	4/3/68	240	2364	1265	.004	.0042	543	51	160	51.7	
31	4/4/68	600	2364	1260	.004	---	---	---	---	---	
32	4/4/68	24	2364	---	.004	---	---	---	---	---	reactor (weak) break
33	4/4/68	206	2364	1255	.004	.0043	427	93	301	51.7	reactor (weak) break
34	4/5/68	50	1124	1250	.0039	---	---	---	---	---	plugged CH_4 meter
35	4/5/68	578	1124	1260	.0039	---	---	---	---	---	splice and trap change
36	4/5/68	280	1124	1255	.0039	.0041	368	72	223	54.2	grey B_4C
37	4/8/68	840	1124	1225	.0039	.0041	606	140	404	53	
38	4/9/68	840	1124	1225	.0039	.004	591	420	506	52.9	last run
		13294									

Overall average tensile strength 396,000 psi

Uncoated Substrate Room
Temperature Strength
UAL 1124: 515 506 485
HS 2364 410

without direct evidence that despite a preheating stage, operated at low red heat, some surface contamination persisted and prevented deposition in localized areas. This is partially based on the line-like appearance of some of these areas which suggests a rubbing or streaking phenomenon, not usually associated with adsorption per se. It remains to be seen if these areas are more subject to damage from diffusing species than the areas which have the characteristic matte-black finish of boron carbide.

Figure 2 shows a longitudinal section of the matte-black boron carbide coating while Figure 2 is a view of one of the silvery-gray areas described above. Figure 4 is a cross section view of a fracture surface of high strength, while Figure 5 shows a low strength fracture surface. The latter two are both spiral breaks with a rather steep pitch compared to material made earlier. The larger fracture area and slower crack propagation which may be associated with this type of surface could explain the rather remarkably high strength of this filament. On the low strength break, a number of sharp radial steps can be seen. These were usually associated with low strength breaks; the lower the strength, the longer the steps appeared to be in the radial direction. These are judged to be fracture phenomena rather than regions of intrusion, diffusion or recrystallization due to the coating. While Figures 4 and 5 do not clearly show the boron carbide coating, Figures 6 and 7 made with the same material, give an ideal of the thickness of the coating, as well as an indication of its uniformity. Figure 7 in particular shows one of the bare areas discussed above.

As in the past, etching and conductivity changes are the only direct evidence that boron carbide has been deposited. The composition and structure of the coating remain unknown due to the fact that only a broad diffuse band is obtained in x-ray diffraction studies. Carbon analyses will be obtained in the near future on material having experimental significance in the composite section of the program.

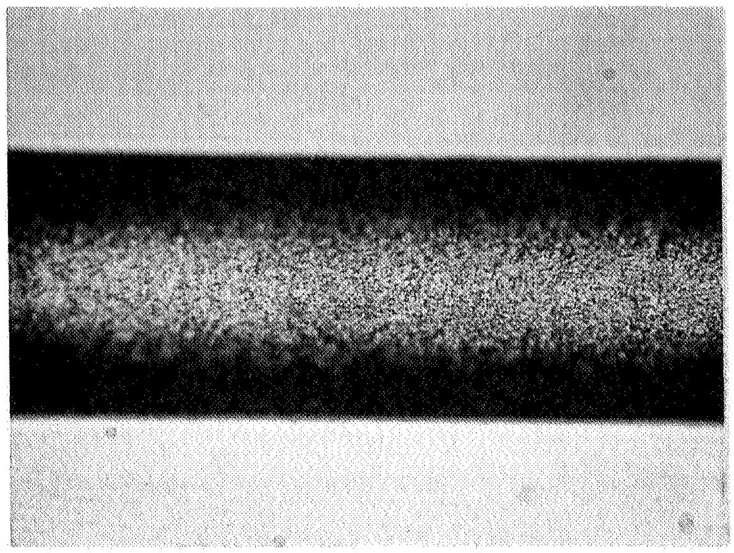

Figure 2. Lateral View of $B_4C/B/W$ Filament (400X)

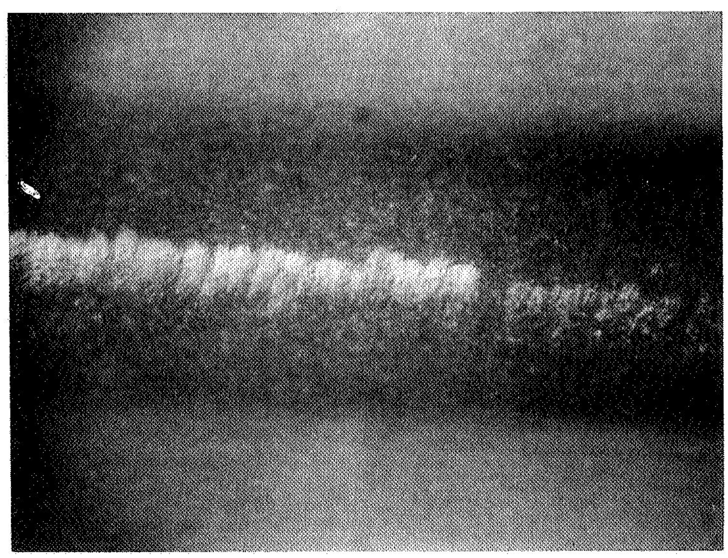

Figure 3. Uncoated Area on $B_4C/B/W$ Filament (400X)

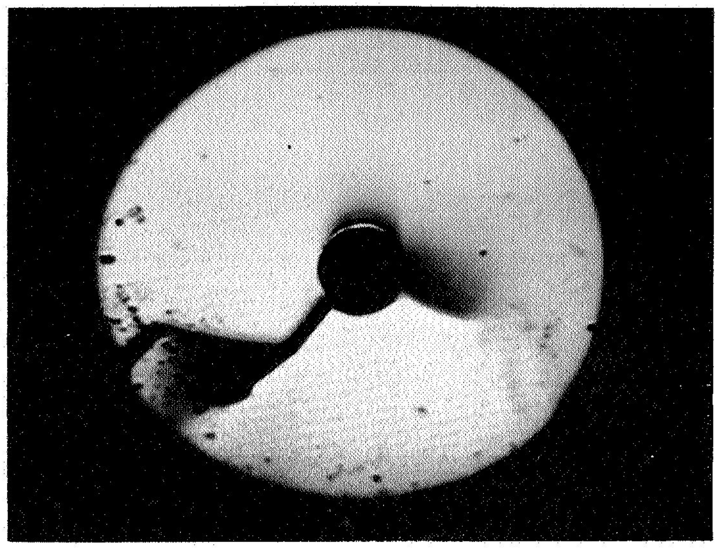

Figure 4. Electron Microprobe Positive Specimen Current Images of Special Fracture Surfaces. High Strength Failure (600X)

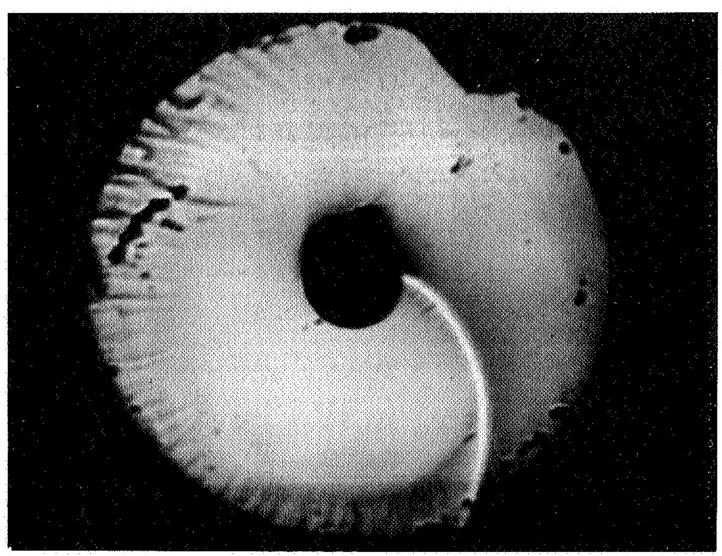

Figure 5. Electron Microprobe Positive Specimen Current Image of Low Strength Failure Showing Radial Steps (650X)

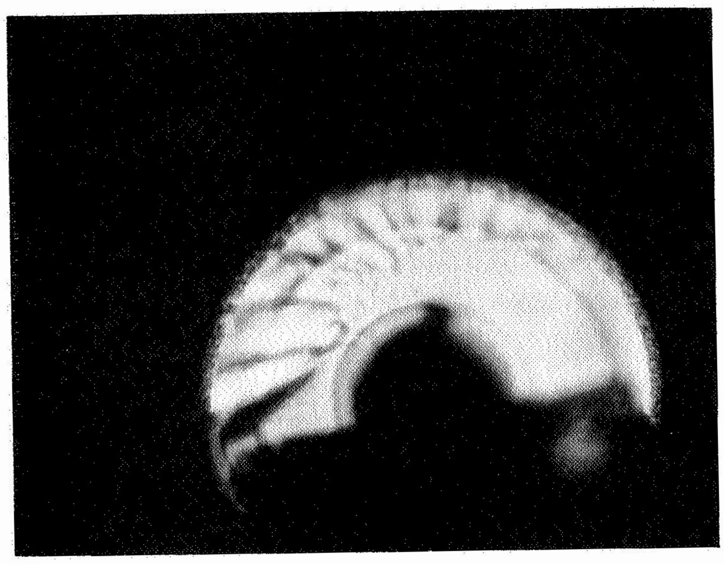

Figure 6. Cross-Section of $B_4C/B/W$ Filament after Etching 1 Hour in H_2O_2 (Run 7). Coating Thickness Approx. .13 mils (593X)

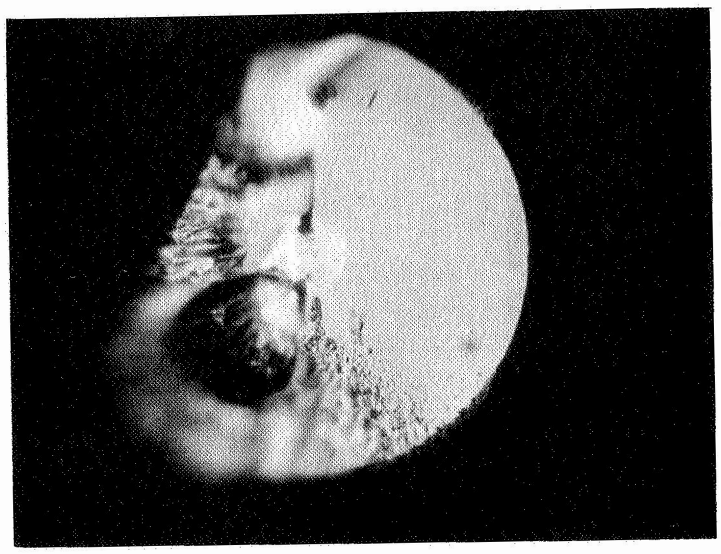

Figure 7. Cross-Section of $B_4C/B/W$ Filament (Run 7) Unetched, Showing Base Area. Tapered Edge Indicates Uneven Deposition, Rather Than Spalling as the Cause. Coating Thickness Approx. .07 mils (593X)

2. $B_4C/B/SiO_2$ Filament

A limited quantity of boron carbide coated boron on silica was also prepared for test purposes. Because of the much higher electrical resistance of this substrate, prepared on a carbon coated silica core by decomposition of diborane, a different power supply circuit was required. Continual runaway heating conditions were encountered owing to the negative thermal coefficient of resistance of boron until large ballast resistors were put in series with the filament. From this point on, deposition characteristics were the same as for the boron on tungsten substrate, using identical conditions.

Although the boron on silica substrate is prepared at much lower deposition temperatures (ca. 750°C) than the boron on tungsten (ca. 1150°C) no pronounced loss in strength was observed as a result of the coating. However, the scatter was much greater on account of the larger scatter in strength values of the substrate itself. Some better than average results are shown below in Table III.

TABLE III. COMPARISON OF TENSILE STRENGTH OF B/SiO_2 AND $B_4C/B/SiO_2$ FILAMENTS

Filament	Tensile Strength (Ksi)		
	High	Low	Avg.
B/SiO_2	350	107	257
$B_4C/B/SiO_2$	396	107	280

The appearance of the filament is generally similar to that of the coated boron on tungsten material as is shown in Figure 8.

B. CHARACTERIZATION OF COMPOSITE MATERIALS

1. Filament Evaluation

Since this program is concerned with an investigation of the factors which control the mechanics, the physical and the chemical behavior of metal-matrix composites reinforced with brittle, discontinuous fibers, it is highly important that parameters which affect this behavior be well

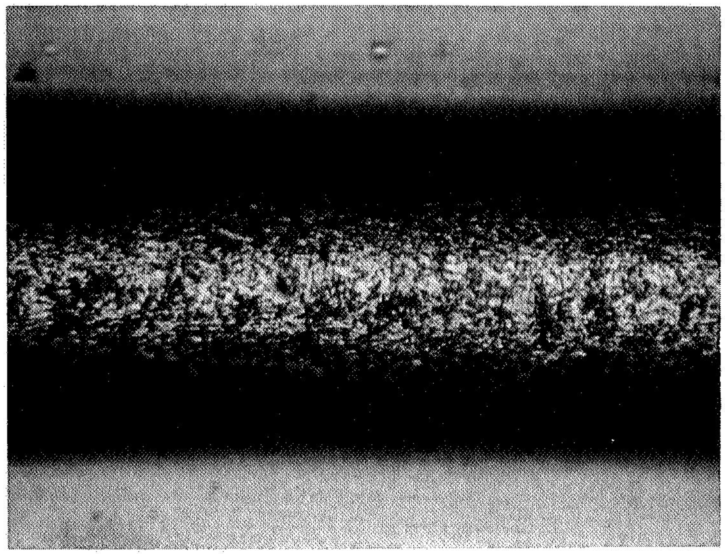

Figure 8. Boron Carbide Coated Boron on Silica (490X)

identified and characterized. The approach used evolves simply from the concept of combining well-characterized brittle fibers with a well-characterized matrix metal and with simple composite test configurations.

The characterization of the variables includes such factors as the average strength and strength dispersion of the fibers, fiber aspect ratio (L/d), fiber strength degradation during processing, and so forth. By systematically varying composite parameters and by comparing the results with theory, either the existing theory will be verified or the theory will be modified to account for the experimental observations. Such understanding will delineate the key variables and their relative importance.

The strength properties of composites containing high modulus, high strength, brittle fibers are primarily dependent on the fiber properties. Therefore, it is essential to measure the strength characteristics of the fibers both before and after fabrication into composites. During this reporting period, the filamentary materials extensively tested were $B_4C/B/W$

and $B_4C/B/SiO_2$. All tests were performed on an Instron tensile machine at a strain rate of 0.02"/"/Min. on specimens of one inch gauge length. A summary of the data is presented in an earlier section. (See Table II).

2. Epoxy Evaluation

During present epoxy-filament composite studies it was necessary to devise a means to adjust the bond strength between filament and matrix. A valid approach would be to vary the plasticizer content of the formulation. Just such an approach was tried. Table IV summarizes the formulation compositions while Figure 9 presents the tensile strength of each formulation at two different strain rates (2"/"/Min. and 0.02"/"/Min.).

TABLE IV. EPOXY NOVOLAC FORMULATIONS STUDIED

Epoxy Designation	DEN 438	PPG 425	MNA	BDMA
PPG (30)*	52**	30	36	1
PPG (36)	52	36	36	1
PPG (38)	52	38	36	1
PPG (40)	52	40	36	1

* Standard formulation
** Numbers in all columns represent quantity parts

It was found that the bond strength could indeed be varied using this technique. However, as discussed in a later section, the crack sensitivity of the more heavily plasticized materials, increased at a much faster rate than the bond strength decreased so that the overall effect was a fracture behavior which did not change markedly.

The problem of varying bond strength independent of epoxy chemistry (and therefore basic tensile strength) was solved, however, by treating the surface of the filaments with graphite or teflon so that intermittent bonds would form. These materials are inert in the novolac formulations and it is to be noted that many other organic or inorganic lubricants or sizings (such as MoS_2, WS_2, etc.) could be equally effective. Thus, a system was devised which can vary the bond strength of the epoxy formulation which had been standardized in previous work.[6] This isolation or separation of

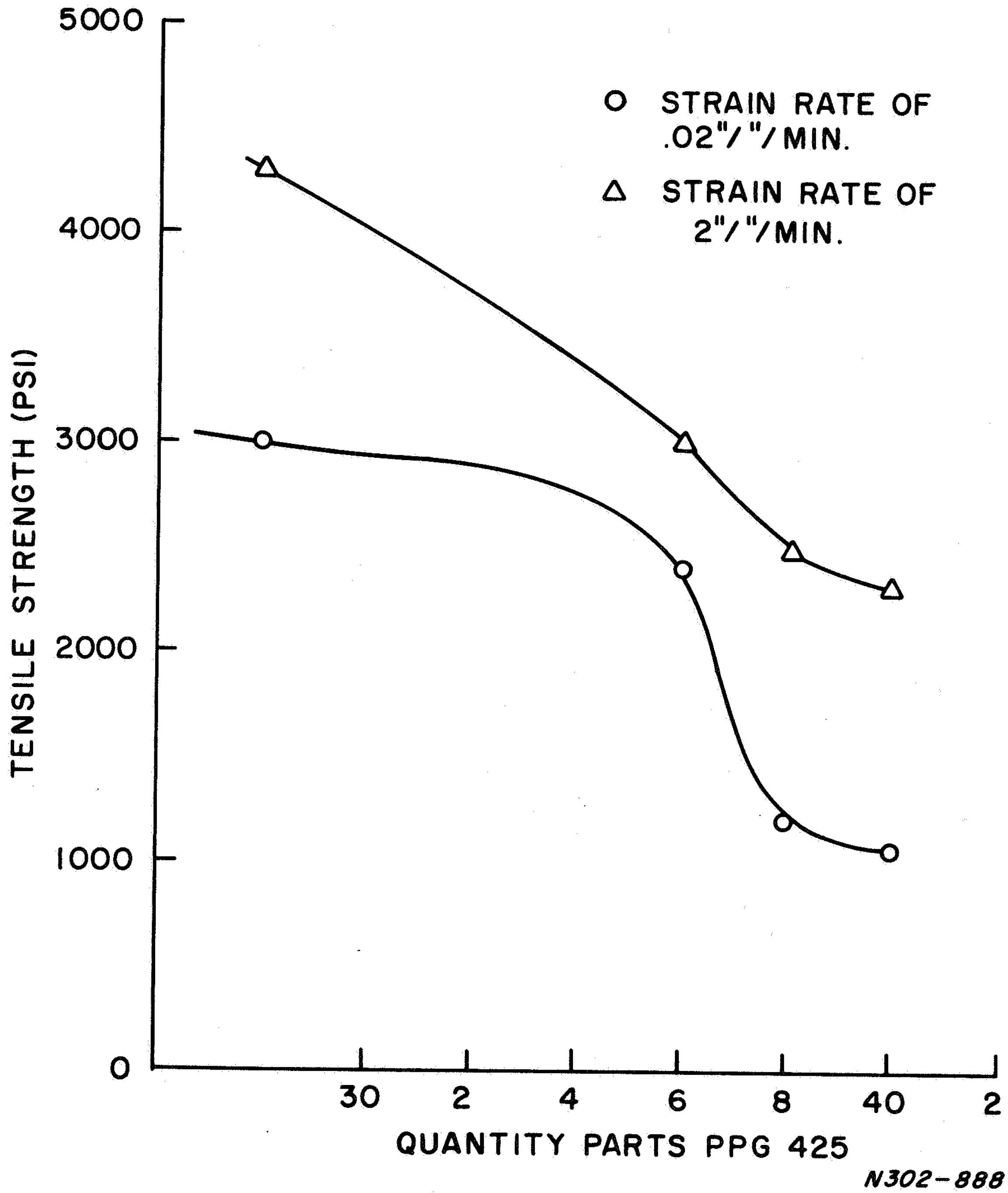

Figure 9. Variation of Tensile Strength of Epoxy Novolac as a Function of Plasticizer Content (PPG425)

the bond strength variable from the many parameters which affect composite strength is an important result of this quarter's effort.

C. ALUMINUM MATRIX COMPOSITE SYSTEMS

The effort in the metal matrix area was directed toward adopting the technique of others[8] to produce $B_4C/B/W$-aluminum test samples which would be suitable for high temperature testing. First attempts to utilize graphite inserts in a graphite mold to form the gauge section of a tensile bar (See Figure 10) failed because of the large difference in thermal expansion between aluminum and graphite which consistently produced tensile failure of the specimen at the fillet on cooling. A modification was made which appears to solve this problem. A 2" long, 1/4" O.D. steel tube (SAE1020) with an I.D. of 0.080" was filled with filamentary material and the assembly was infiltrated with molten aluminum at 700°C in a hydrogen atmosphere. A one inch gauge, 0.080" in diameter section was then ground from the center of the composite casting forming a usable specimen geometry. (See Figure 11).

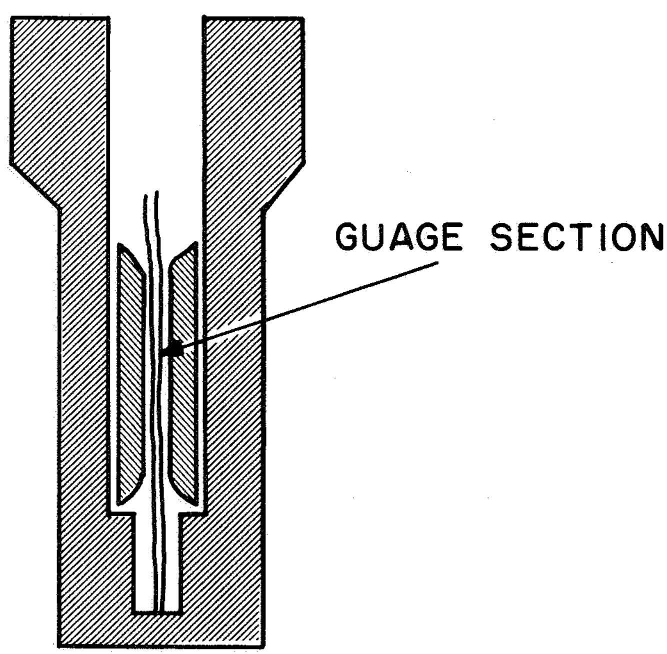

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Figure 10. Schematic Diagram of Graphite Mold - Graphite Insert Assembly

Specimens formed by this method will be used for high temperature testing including uniaxial tension, creep and fatigue.

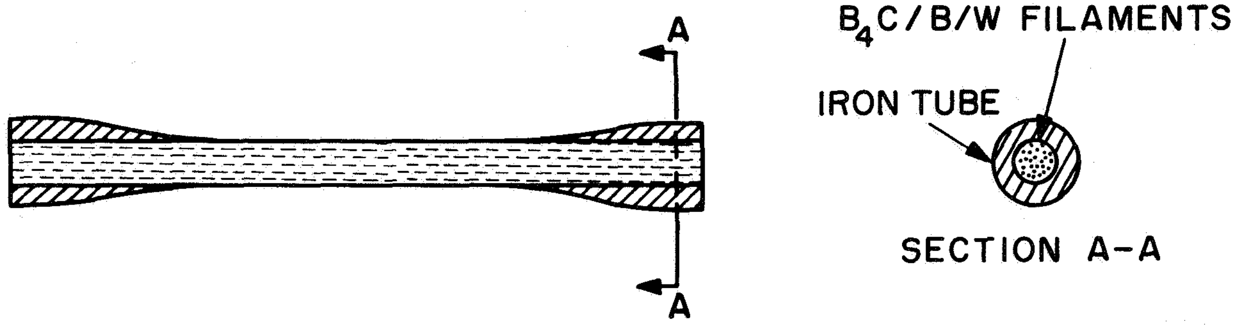


Figure 11. Sketch Showing Fabrication Technique for Al-B_4C/B/W Tensile Bars Suitable for High Temperature Testing

D. EPOXY NOVOLAC MATRIX COMPOSITE SYSTEMS

1. Mechanical Compatibility Model

An attempt has been made to develop a simple schematic model for the graphic rationalization of expected composite behavior, and this is shown in Figure 12. Most of the detail of this model is based on the mechanical behavior and fracture phenomenology of simple filament-epoxy specimens tested during the course of this contract. The purpose of the model is to provide a qualitative frame of reference within which (1) a wide variety of test results can be rationalized and (2) more clearly critical experiments can be designed.

The ordinate on the diagram (Figure 12) represents the mormalized composite strength which would be expected from the rule of mixtures in its simplest form, as given by:

(1) $\sigma_c = \sigma_m (1-V_f) + \sigma_f V_f$ where σ_c, σ_m and σ_f are the strengths of the composite, the matrix and the filament, respectively, and where V_f is the volume fraction of the reinforcing filament.

The abscissa of the diagram shows many of the parameters which determine when and to what extent the rule of mixtures will be obeyed. The interdependence of many of the important variables has been quite evident in much of the experimental work previously reported (see, in particular, the 5th Progress Report)[9] and is also evident in the work on bonding described later in this report. For purposes of ready allusion to the interrelation of fundamentally mechanical, as distinct from chemical, aspects it seems warranted to make use of the phrase "mechanical compatibility". One might say that mechanical compatibility is satisfactory when premature filament failures do not adversely affect the ability of the matrix to redistribute the load in the manner tacitly assumed by the rule of mixtures. Some work has been started in an attempt to develop an analytic formulation of mechanical compatibility by which the rule of mixtures can be re-stated in a more general form. In the interim, these mechanical parameters have been categorized as relevant to (a) bond and matrix properties; (b) filament properties; (c) composite geometry; and (d) test conditions.

The directional arrows on the mechanical variables (abscissa, Figure 12) point in the direction of an increase in the property, dimension, etc. The effect of some of these variables will now be discussed.

At the top of the diagram, three regions of composite behavior are indicated: (1) Bond Limited; (2) Filament Limited; and (3) Matrix Limited. By definition, a Bond-Limited composite does not utilize the average strength of the reinforcing filament, because the bond fails at a stress below that required to break filaments of average strength. That is, although the matrix is capable of redistributing the load, the bond is too weak to transmit the load from the broken filament to the matrix. Fracture is characterized by only a few breaks per filament (at the weaker regions) and extensive filament pull out. Filament-Limited behavior is, of course, the most desirable type

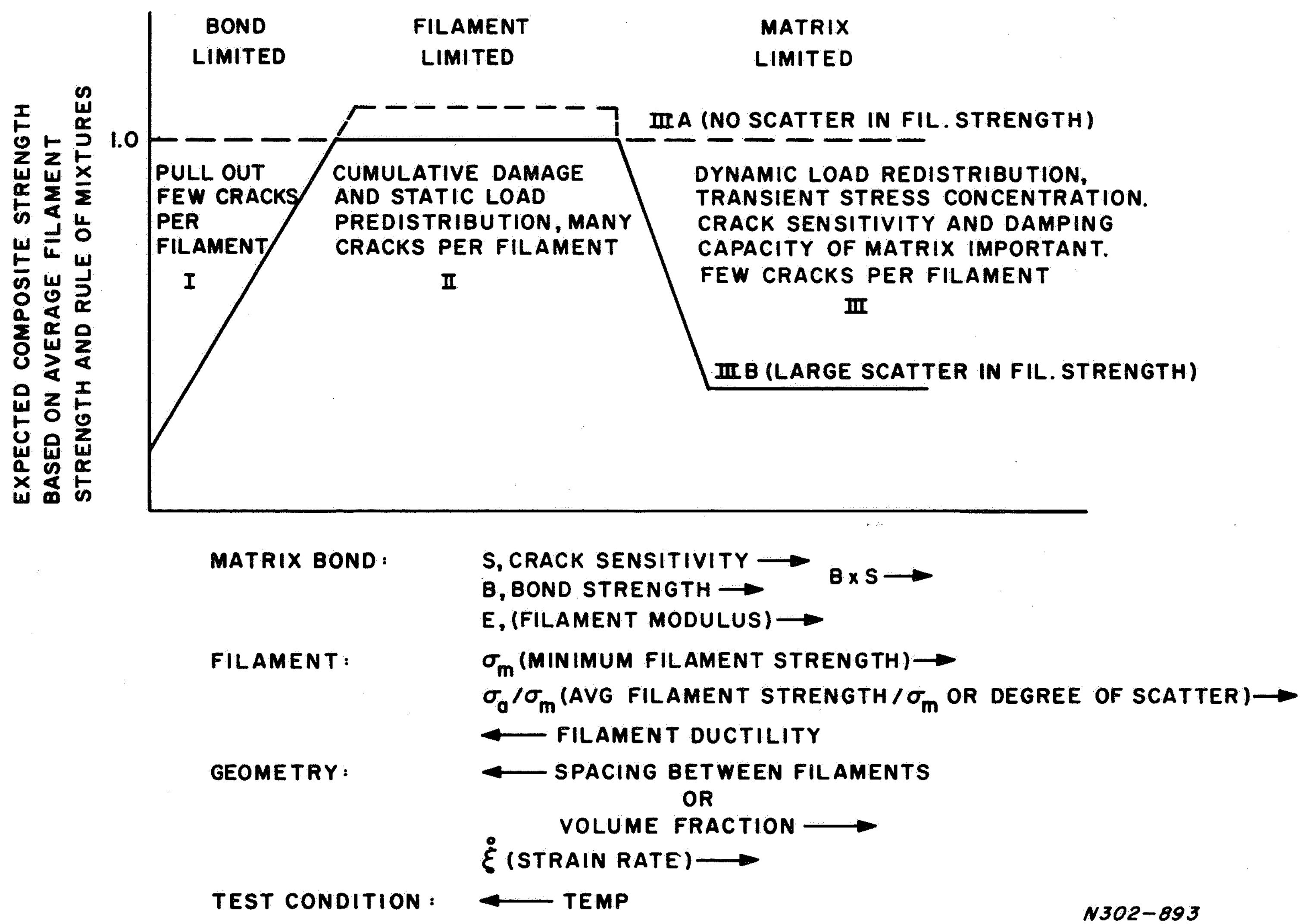


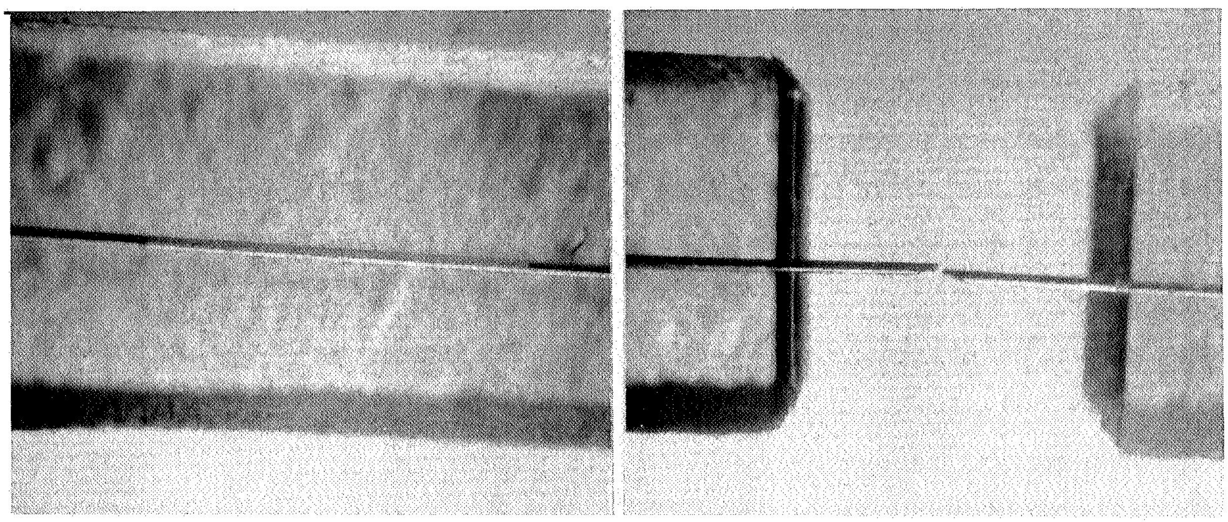
Figure 12. A Schematic Model for the Graphic Rationalization of the Effect of Materials Properties, Specimen Configuration and Test Conditions on the Performance of Composites

of behavior because the strength of the composite reflects, as predicted by the rule of mixtures, the average strength of the reinforcing filament. Such composites fail by cumulative filament damage (many cracks per filament) and are free of substantial matrix contribution to premature failure. This is not only inherently advantageous but it also is especially amenable to statistical sophistication in performance predictions. In this connection, Figure 12 shows a Filament-Limited region (IIA) above that predicted on the basis of average filament strength. This takes into account the fact that the strength of filamentary materials often increases as the gage length decreases. Thus, after many non-catastrophic failures, the gage lengths remaining in a composite may be stronger than those used in characterization tests of the filament. Matrix-Limited behavior is undesirable because the composite performance is often limited by the weaker of the two components, the matrix. Numerous examples of the loss of matrix integrity in filament-epoxy specimens have been discussed during the course of this work. Briefly recapitulated, the matrix may redistribute the load, arising from filament failure, in a manner (say, cracking) which adversely affects the strength of the composite. Composite failure is frequently brittle and the relatively few fractures per filament show that strength utilization is less than required. In Matrix-Limited behavior, composite strength is limited by certain "defects" rare enough to be regarded as insignificant in ordinary statistical characterization of separate composite components. The upper dashed line in the Matrix Limited region (IIIA) in Figure 12 shows that the matrix limitations are of little consequence if the filament strength is scatter-free.

2. Bond Strength - A Compromise

Much of the previously reported work done on filament-epoxy specimens has been concerned with limitations of the matrix capacity to redistribute load in the vicinity of filament failure in a manner consistent with the assumption of the rule of mixtures. In most instances, the filaments have been sufficiently well-bonded to insure that the energy released upon filament failure was transmitted through the bond and into the matrix. During the last quarter, experimental work has been designed to demonstrate the critical nature of the filament-matrix bond, which is important for two reasons: (1) an understanding of the critical nature of the bond is necessary for a general understanding of composite performance, as will be discussed later; and (2) unbonding is a rather common practical problem in metal matrix composites and has lead to considerable efforts toward improved bonding.

Since unwanted unbonding had not been a major experimental difficulty in filament-epoxy specimens, special attempts were made to reduce bond strength in order to test the hypothesis that the maximization of bond strength may not be always necessary or even desirable. Figure 13 shows failure



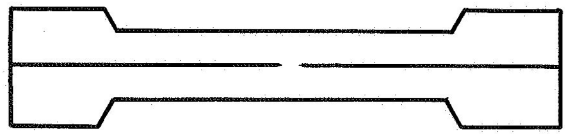
Two filament failures with extensive unbonding and filament pull-out and no filament-associated matrix cracking. Specimen failure originated in matrix at edge of specimen.

Figure 13. Profile of Failures in Teflon Coated Single B/W Filament-Epoxy Specimen Tested in Tension at $\dot{\epsilon}$ = 2"/"/Min. (Spec. 715, 17X)

in a single filament-epoxy specimen in which the filament had been teflon coated to drastically reduce the bond strength. Neither of the two filament cracks propagated into the matrix; long unbonded regions were evident, the extent of pull-out being evident from the fact that two ends project from the fracture surface. The final fracture started in the matrix at the edge of the specimen. As will be discussed later, the mechanical behavior of this specimen was similar to that of plain epoxy.

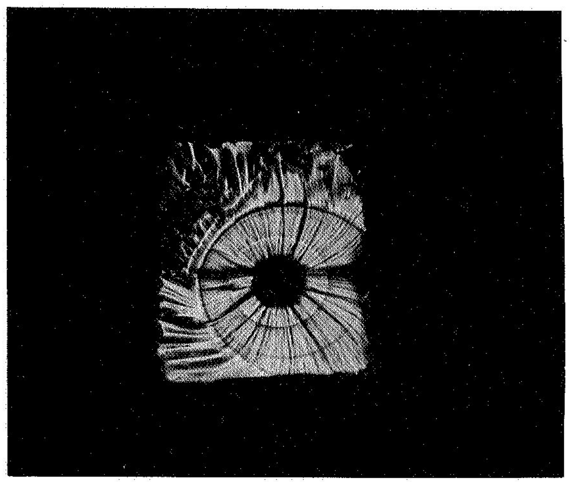
Figure 14 shows the fracture surfaces and profiles of single discontinuous filament-epoxy specimens. When both segments of the filament were graphite coated (Spec. 708, Figure 14) failure was by the slow propagation of a matrix tensile crack from an end of one of the filament segments. The other cracks in the filament segments resulted in local unbonding and/or slowly propagating (non-catastrophic) matrix tensile cracks; when closely coupled; the alternation (of unbonding and cracking) may be-characterized as a "slip-stick" fracture mode. This specimen was approximately as strong as plain epoxy (also true in tests at $\dot{\epsilon}$ = 2"/"/Min.) and considerably stronger than the other discontinuous specimen (No. 712) having only one of the segments graphite coated. The latter failed in a brittle manner by the rapid propagation of a matrix tensile crack from a crack in the uncoated filament (as is evident in Figure 14); that is, this specimen was not significantly different from a continuous filament specimen similarly tested (see Spec. 518, Table VIII and Figure 6, 5th Quarterly Report).[9] In regard, then, to the mechanical behavior and fracture mode, the fact that these specimens had discontinuous, rather than continuous, filaments was of less importance than the bond strength.

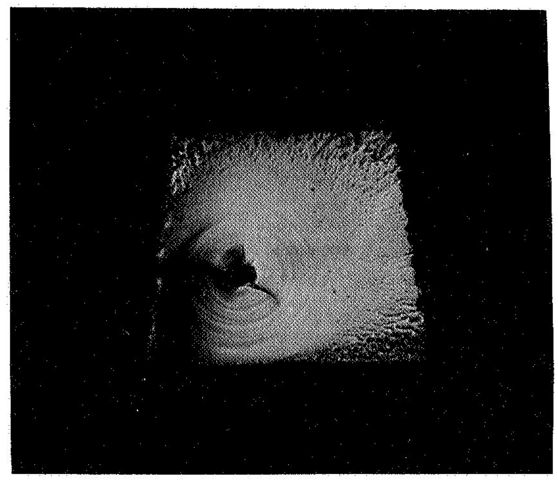
From these results it seems reasonable to infer that discontinuous composites will be weaker than continuous composites when bond strengths are very low. At bond strengths inherently high enough to load the filament to fracture, the crack sensitivity of the matrix would become critical. A ductile crack originating at an early filament failure might not be as damaging as a larger one already present at a filament end in a discontinuous composite, and it would be weaker than a comparable continuous composite. However, when the bond strength is high enough to propagate the filament failure into the matrix in a brittle fashion, there would be little reason to expect the two kinds of composites to behave differently. This, of course, is not definitive because so many of the other variables (see Figure 12),



Both Filaments Graphite Coated
σ = 3120 psi (Spec 708)

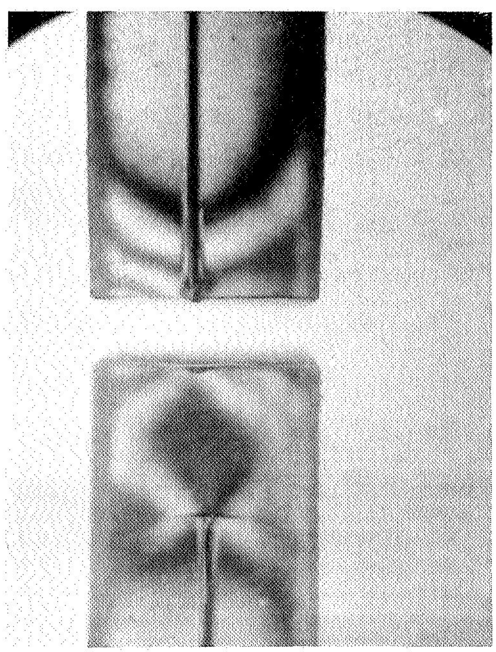
One Filament Graphite Coated
σ = 2650 psi (Spec 712)





Fracture Surfaces (17X)

Failure in Uncoated
Filament Generated
Catastrophic-Matrix Crack



FRACTURE PROFILES

17X

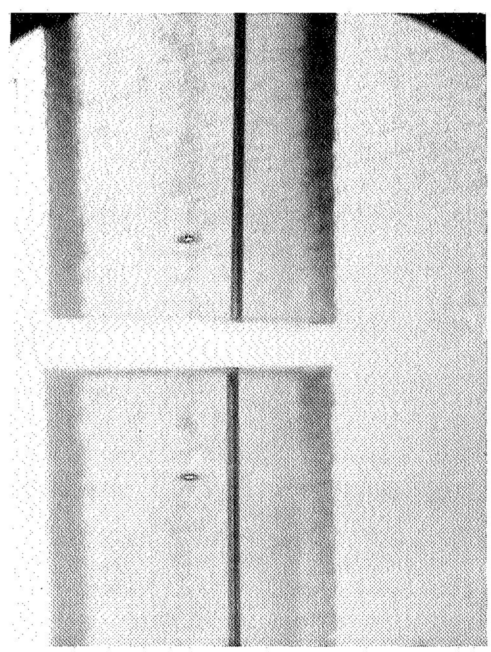
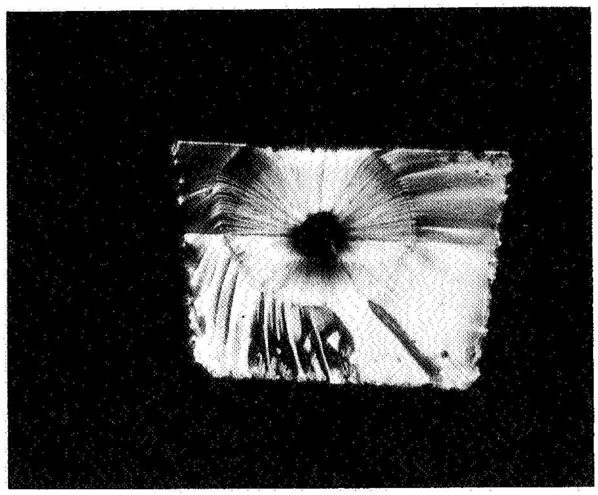
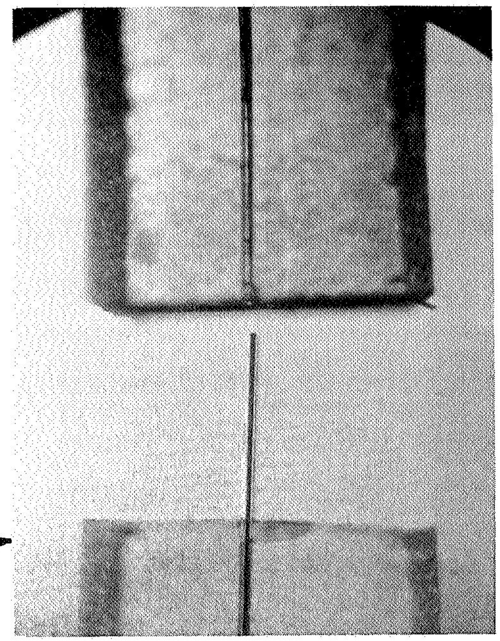


Figure 14. Discontinuous Single B/W Filaments Tested at $\dot{\epsilon}$ = 0.02 in/in/min

which influence expected composite behavior, can also be expected to have relevance for the discontinuous-continuous comparison. The limited amount of evidence and many of the lines of reasoning that come to mind suggest that discontinuous composites are most likely to be as strong as continuous composites when both are weak and brittle (Region III, Figure 12).

Duplicate specimens (each containing a simple continuous graphite coated B/W filament in epoxy) were tested in tension at 2"/"/min., a strain rate which always results in weak brittle specimens if the filaments are uncoated (that is, well bonded). The fracture surfaces and profiles are shown in Figure 15. In addition, each specimen had five non-catastrophic filament failures which exhibited the "slip-stick" fracture mode, an example of which is shown in Figure 16. It is evident (Figure 15) that considerable unbonding was associated with the catastrophic failure in Spec. 701; eventually it stuck enough to generate the fatal, slowly propagating, tensile crack (perhaps in a region of incomplete graphite coating). In the case of Spec. 702, two matrix cracks (associated with the "slip-stick" region evident in the profile in Figure 15) were in the process of growth. However, before either of these could propagate sufficiently to separate the specimen, a matrix crack originating at the specimen edge (see fracture surface, Figure 15) intervened catastrophically. The mechanical behavior of these specimens was similar and superior to specimens exhibiting unlimited unbonding (e.g., Figure 13) or very good bonding (e.g., Figure 14, Specimen 712).

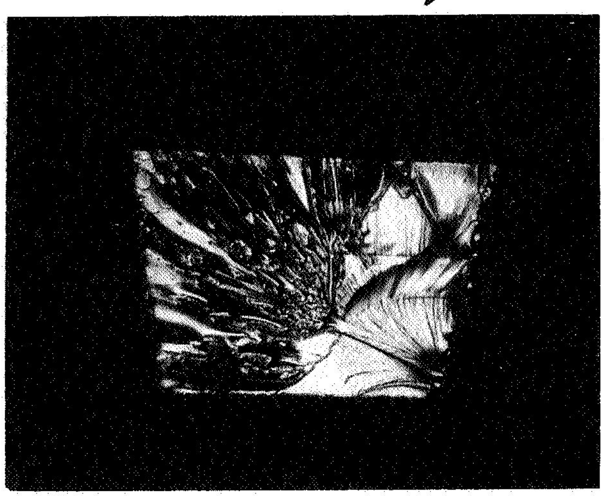


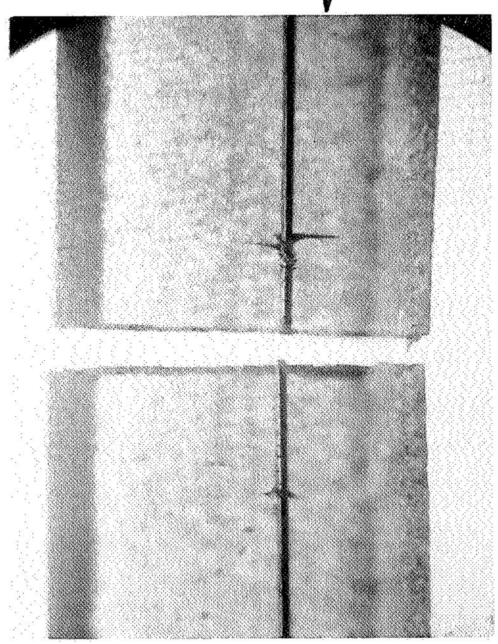


No. 701

Note Unbonding
and Followed By
Sticking and Slow
Matrix Crack
Growth to Failure

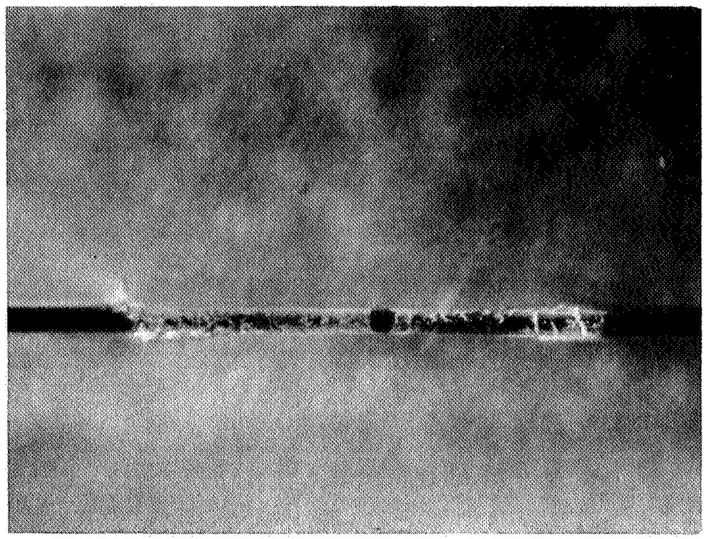
Note Failure by Edge Crack Before
Extensive Growth of Matrix Cracks
Associated Unbonded Filament





No. 702

Figure 15. Graphite Coated, Continuous Single B/W Filament Tested at $\dot{\epsilon}$ = 2 in/in/min (17X)



Note combination of unbonding and small matrix cracks

Figure 16. A Typical Fracture Profile of one of Five Non-Catastrophic Cracks in Graphite Coated B/W Filament-Epoxy Specimen Tested At $\dot{\epsilon}$ = 2 in/in/min. (Spec. 701, 35X)

The relationship between tensile behavior and bond strength for single filament-epoxy specimens is illustrated by the stress-elongation curves in Figure 17. The tensile tests were made at a strain rate of 2"/"/Min., a rate known to result in weak brittle behavior for well bonded specimens (see Table VIII and Figure 19, 5th Progress Report.).[9] As expected, the well-bonded specimen (uncoated filament) failed at the first filament failure and was both brittle and weak relative to the plain epoxy. This specimen was "Matrix Limited" and is, thus, an example of failure in region III of the model (Figure 12). Spec. 715, having the teflon coated filament, exhibited two filament cracks and unlimited unbonding (Figure 13). It was slightly weaker than the plain epoxy (but not brittle) and can be regarded as an example of failure in region I of the model (Figure 12). Spec. 701 exhibited cumulative damage (many filament cracks prior to failure) and was somewhat stronger than the plain epoxy and may be regarded as an example of failure in region II of the model (Figure 12).

It is evident from these results that the slip-stick mode of failure associated with early filament failure in graphite coated filament is preferable to either unlimited unbonding or to catastrophically "good" bonding. For this particular set of circumstances, the graphite coating is the best compromise bond. First, the bond is weak enough so that filament failure does not generate a rapidly propagating catastrophic matrix tensile crack. Therefore, the load can continue to rise as the filament breaks up and this insures some utilization of the stronger portions of the filament.

This point is, of course, crucial if "real" composites are to reflect the average rather than the lowest filament strength. Second, the bond is strong enough to "stick" and prevent the unlimited unbonding which also precludes load redistribution. In summary, the "slipping" prevents catastrophy and the "sticking" is necessary for effective load redistribution.

While the foregoing results are definitively applicable only to these specimen materials and configurations, they serve to emphasize the point that bond strength should be an appropriate, not necessarily the maximum attainable, value. The bond strength required will depend upon the matrix crack sensitivity, and it will be noted that the product of the two is identified as an important parameter in the model (Figure 12).

There are ambiguities in the nature of materials that may frustrate attempts to make statements that are both rigorous and general. For example, in the case of epoxy novolac, there is an ambiguity in the term "matrix crack sensitivity". In previous discussions, (earlier progress reports) it was pointed out that this epoxy exhibits two kinds of tensile cracks. One propagates very rapidly, creating smooth surfaces; and may propagate to specimen failure while the load-elongation curve remains linear; therefore, it is logical to refer to this kind of crack as "brittle". The other kind of matrix crack propagate less rapidly or even quite slowly, creating linearly marked surfaces, and can do so during non-linear load-deflection behavior; this kind of crack propagation has, from time-to-time, been characterized as "ductile". When, by a change in formulation, the epoxy is made more

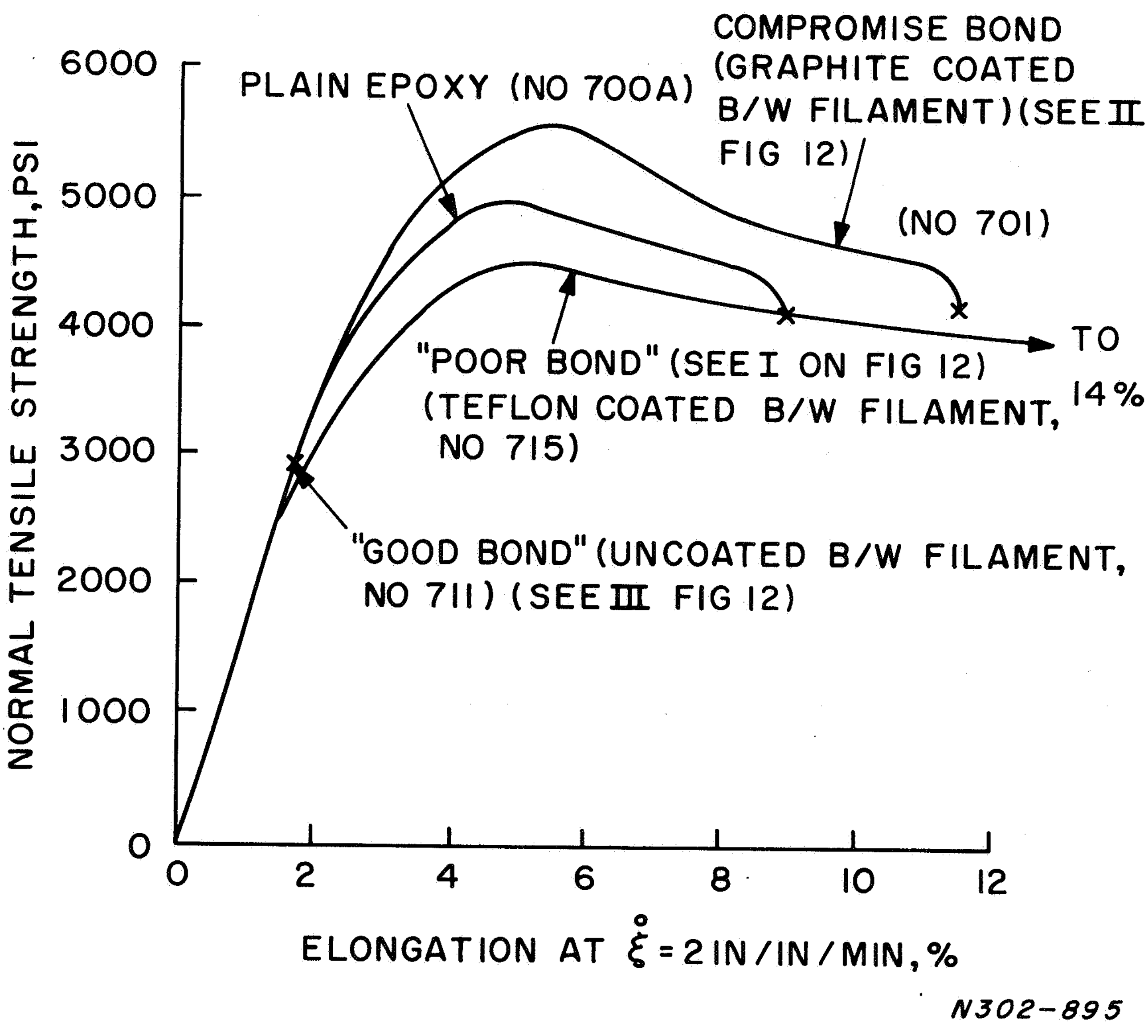


Figure 17. The Effect of Bond Strength on the Tensile Behavior of Single B/W Filament-Epoxy Novolac Specimens

flexabilized, it appears to become more resistant to the formation and/or propagation of "brittle" cracks but less resistant to the growth of "ductile" cracks. These divergent characteristics lead to some ambiguity in some early attempts to modify bond strength by changing epoxy formulation. The expedient of coating the filaments with graphite or teflon worked, because the bond strength could be changed independently of either of the two matrix crack sensitivities. The situation might be considerably more difficult to evaluate and control in metal matrix composites if, for example, bond-enhancing coatings diffuse into the matrix and adversely affect its capacity for plastic deformation or its crack sensitivity.

3. Summary Remarks on Mechanical Compatibility

A study of the behavior of simple filament-epoxy specimens in uniaxial tension has been used to develop a generalized model (Figure 12) for explaining and predicting many effects of material properties, specimen configuration and test conditions on composite performance. It is abundantly evident that the many variables involved are strongly interrelated; therefore, it promises to be virtually impossible to predict composite performance from conventional data obtained by testing the separate components of an intended composite. Chemical compatibility is recognized to be an important attribute of successful composites, and it seems warranted to assert that what may be called mechanical compatibility is of comparable importance.

Given, on the one hand, a general understanding of the mechanical compatibility problem via the model and, on the other hand, an almost certain knowledge that highly specific information will be required to produce good composites using the filament-matrix systems, it seems warranted at this time to divert an increasing amount of effort to the study of other filament-matrix systems of interest.

III. FUTURE WORK

Further study in the area of continuous B_4C filament production will consider lower temperature deposition systems. The characterization of composite component materials is an important and necessary part of this program and will continue.

Emphasis will continue to be placed on the aluminum matrix/continuous-filament composite systems and on high temperature stability tests such as heat treatment, creep, and tensile tests. Specimens have been designed to further substantiate the results and conclusions made during this work period.

Further extensive work in the epoxy matrix-filament is not contemplated. However, as a consequence of bonding efficiency studies, testing of both continuous and discontinuous composites in single and multiple filament arrays to further clarify these observations may be warranted.

ACKNOWLEDGEMENTS

The authors acknowledge the assistance, helpful discussions, and suggestions of Mr. W. Laskow and Dr. W. H. Sutton.

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APPENDIX

INTERMITTENTLY BONDED FILAMENTS

In recent tests aimed at controlling the bond strength between filament and matrix, the mechanical application of graphite to the surface of boron filament has provided some interesting results. The "corn cob"-like surface of the filament causes nonuniform application of the graphite on the filament with a resulting pattern of intermittent coated and uncoated regions. This condition provides bonding in the low spots while the high points are shielded from the matrix by the graphite coating.

To better appreciate the experimental results it is important to analyze the way in which the reinforcing mechanism is influenced by this intermittent coating of the filament.

Figure 18 shows the surface of a boron filament at high magnification and the knobby appearance is quite representative of all points along the length of the filament.

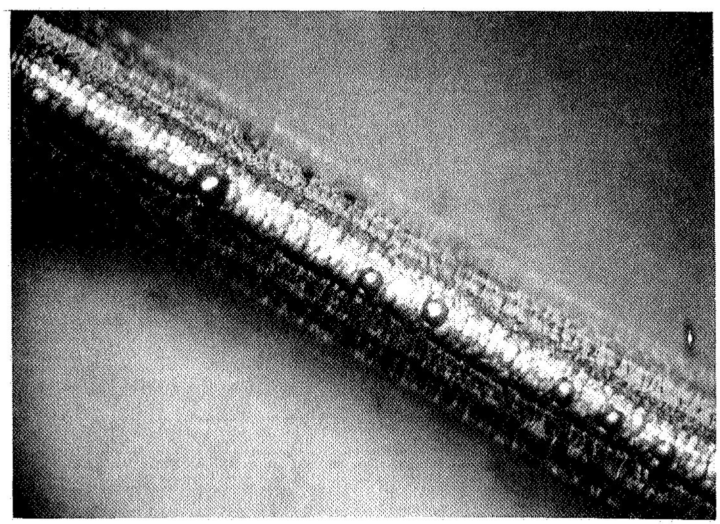

Figure 18. Photo of "corn-cob" surface (202X)

The usual model used to describe the shear stress distribution at the interface in a uniformly bonded filament is shown in Figure 19. Here the distribution of the shear stress is assumed to be continuous along the interface between filament and matrix reaching its highest values near the ends.

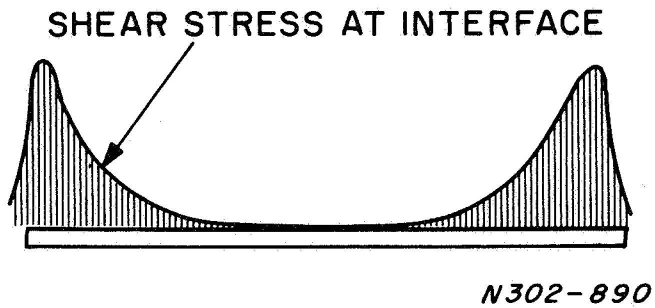

Figure 19. Distribution of shear stresses in a uniformly bonded filament

Actually there are probably local variations in the shear stress distribution which result from surface imperfections and foreign materials such as minute dirt particles which are present on the surface. These can be considered of secondary importance however, compared to the case of the graphite coated filament where relatively large parts of the surface are prevented from bonding. In the simplest model of an intermittently bonded interface we can construct the condition shown in Figure 20. Here the shear

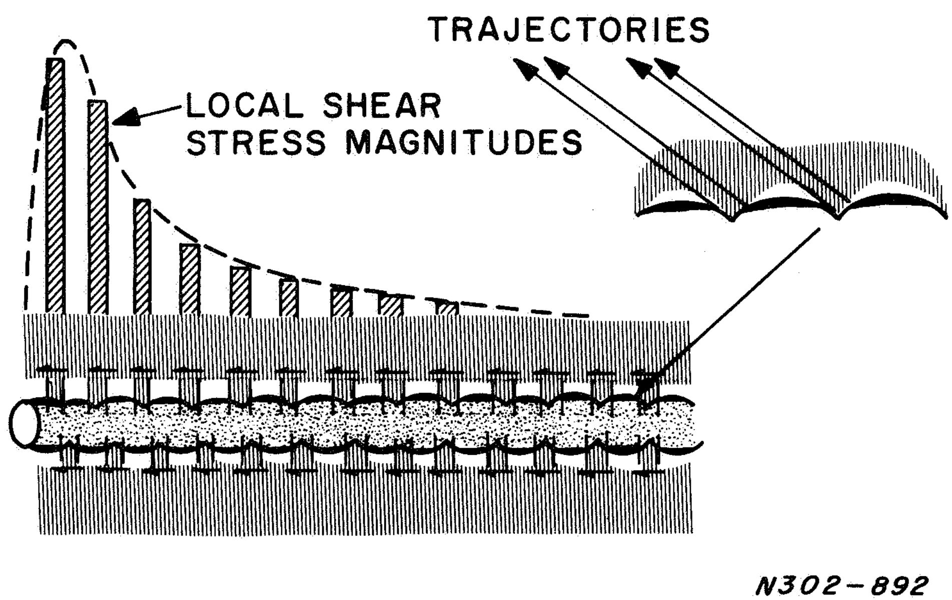

Figure 20. Model of intermittently bonded filament

loads are considered as a series of concentrated forces rather than the continuous distributed forces assumed previously. This has the effect of concentrating the stress trajectories in the regions of bonding and increasing the shear stress at these sites. As each bond area fails its effect on the adjacent areas is dampened to some extent by the unbonded region between them. This condition tends to inhibit a continuous and sudden crack growth mechanism both at the interface and in the matrix (included cracks).

Now consider what happens when the filament fractures. The fracture may occur at any point in the loaded region and the matrix being only partially bonded at the filament fracture site, is not as suddenly influenced by the fracture as in the continuously bonded condition. Consider Figure 21. At point A there is no bond to initiate the sudden crack and at point B the matrix has no reentrant corner to make it crack sensitive.

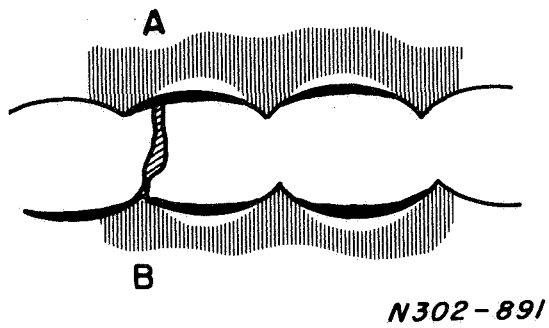

Figure 21. Details of intermittent bonding and its effect on matrix crack sensitivity (schematic).

Further, one can apply a stress concentration argument to the incidence of cracking in the matrix adjacent to a filament break. First consider what happens in the continuously bonded filament shown at the left of Figure 22. The immediate redistribution of load requires very high shears on each side of the break at points A and B. These are very close to the crack and quite high, causing the matrix to experience very high stress concentrations at the point of the break. In the intermittent bond condition, shown at the right of Figure 22, the regions immediately adjacent to the fracture site are not bonded and therefore the new shears which are applied to the matrix at A and B are further away. Distribution of the new local matrix stress over a greater length L in the matrix causes less stress concentration at the filament fracture site and therefore minimizes the possibility of a matrix crack.

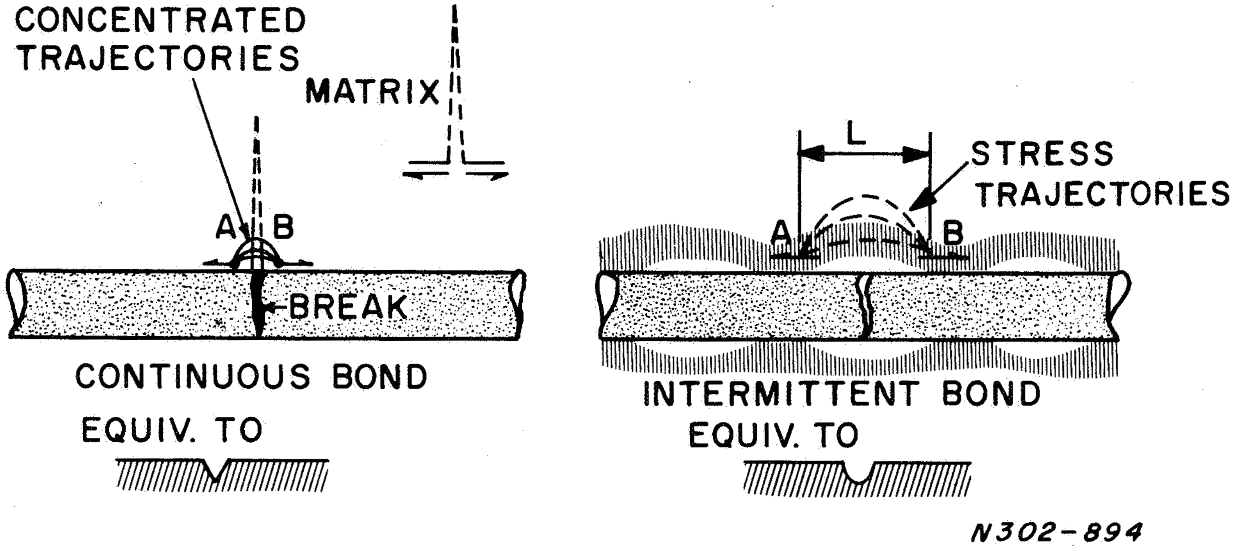

Figure 22. Distribution of stress trajectories as a function of bonding (schematic)